

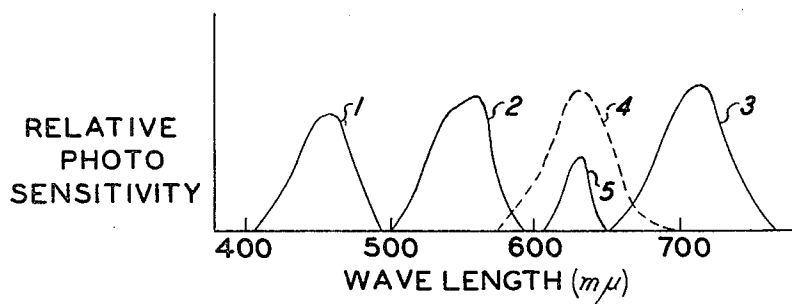
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ELECTROPHOTOGRAPHIC PROCESS FOR MULTICOLOR REPRODUCTION

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ELECTROPHOTOGRAPHIC PROCESS FOR MULTICOLOR REPRODUCTION

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9 Claims

ABSTRACT OF THE DISCLOSURE

Reproduction of a multicolor original in an electrophotographic development employing superimposed development of multiple electrostatic latent images present on an electrophotographic photosensitive layer which is provided with low photoconductivity for a certain wavelength region, and has increased photoconductivity in at least a part of the remaining wavelength region. At least one development is obtained with a toner having photoconductivity for light of the wavelength region in which the electrophotographic level has low photoconductivity.

BACKGROUND OF THE INVENTION

This invention relates to imaging systems and more particularly to electrophotographic processes employing multiple, superimposed development techniques.

Color electrophotography with multiple development techniques is capable of producing color reproductions by the following exemplarily procedures. A suitable photoconductor such as substantially white zinc oxide photosensitive paper. Electrofax paper for example, is electrostatically charged uniformly in the dark, then exposed through a green filter to an imagewise projection of a color image to form an electrostatic latent image on the photoconductor. The electrostatic latent image is then developed with magenta color toner to form a magenta colored image corresponding to said electrostatic latent image. The zinc oxide photosensitive paper is again electrostatically charged uniformly in the dark and then exposed through a red filter to an imagewise projection of a colored image in register with said magenta developed image to form a second electrostatic latent image which second image is developed with cyan colored toner. Similarly, the zinc oxide photosensitive paper is again electrostatically, uniformly charged in the dark and then exposed through a blue filter to an imagewise projection of a colored image in register with said magenta and cyan developed images to form a third electrostatic latent image which is then developed with yellow toner.

This conventional electrophotographic process with superimposed development to obtain images of cyan, magenta and yellow, respectively, is capable of producing multicolor images by employing toners of different color. The sequence of exposures through colored filters in this multiple development process may be performed in any suitable sequence other than the green, red and blue sequence recited above.

While capable of producing color prints, the reproduction of multicolor prints of very high quality is difficult because of the inherent limitations in the available cyan, magenta in yellow toners. An ideal cyan toner should absorb only red light and magenta should absorb only green light and yellow should absorb only blue light. In practice, however, only the yellow colors are reasonably close to being ideal. Cyans in addition to absorbing red light also absorb heavily in the green and to a lesser extent in the blue. Magentas in addition to absorbing in the green also absorb heavily in the blue region. These de-

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ficiencies in available colors results in a serious degradation of color image quality. This undesirable absorption of the cyan and magenta toner images has been largely compensated for by techniques known as masking in which the density of a particular toner, i.e., cyan, magenta or yellow is dependent not only upon the brightness of its complementary color in the original subject to be reproduced, but also and to a lesser extent is dependent on the brightness of one or both of the other primary colors. In a conventional masking technique, a red color separation positive may be bound in register with a green separation negative to form a corrected electrostatic latent image. The density of the magenta toner which is deposited in response to the electrostatic latent image and which is primarily intended to absorb green is decreased in areas of the print where the cyan color occurs. It may be noted that the cyan color which is formed from the red separation negative has an unwanted absorption in the green part of the spectrum. In this way, the total green absorption of the print is made to more faithfully correspond to the amount of green in the original scene. Similarly, a weak green color separation positive is made bound in register with the blue separation negative and the combination used to form the yellow color. In areas where the magenta toner is intense and contributes unwanted blue absorption, the intensity of the yellow color is correspondingly decreased.

This masking method which provides correction for undesirable absorption of cyan and magenta toner images during the multiple development procedure for reproducing an original image is incapable of completely correcting the undesirable absorption. As a result, improper scale reproduction or reproductions with excessive highlight or shadow areas are obtained. Experience has proved that it is difficult to devise a masking method capable of providing precalculated correction for undesirable absorption.

In addition, this masking technique is extremely complex and tedious necessitating the handling of both color separation, positive and negatives, in perfect registration for each of three exposures.

SUMMARY OF THE INVENTION

It is, therefore, an object of this invention to provide a developing system which overcomes the above noted deficiencies.

It is another object of this invention to provide a new masking method.

It is another object of this invention to provide a simplified masking method.

It is another object of this invention to provide a masking method which provides improved correction for undesirable absorption of light.

It is another object of this invention to provide a color electrophotographic development system which produces multicolor images with reduced highlight and shadow areas.

It is another object of this invention to provide a color electrophotographic development system capable of producing improved color images.

It is another object of this invention to provide an electrophotographic development system capable of producing multicolor images by multiple development techniques.

The above objects and others are accomplished, generally speaking, by providing an electrophotographic development system employing superimposed development of multiple electrostatic latent images present on an electrophotographic photosensitive layer which is provided with low photoconductivity for a certain wavelength region or portion of light but which possesses increased photoconductivity in at least a part of the remaining wave-

length range. The electrophotographic photosensitive layer is sequentially charged, imagewise exposed and developed by well known techniques for multiple imaging sequences. For example, an electrostatic latent image resulting from exposure to a first primary color may be formed on the photosensitive layer and developed with a toner complementary to the primary color. In a similar fashion, succeeding developments of electrostatic latent images resulting from exposure to primary colors are accomplished with complementary toners. When exposing through color separation negatives the toner is the complement of the radiation of exposure. At least one development is with a toner having photoconductivity for the light of the wavelength region or portion in which the photosensitive layer has low photoconductivity. After development with the photoconductive toner during the first development step and before development with a toner during the second development step, the photosensitive layer is subjected to a flush exposure with light of the wavelength region of light for which the photosensitive layer has low photoconductivity. The flush exposure may be completed before or after the second exposure step following the second charging step.

This color masking method in an electrophotographic process in which the sequential procedure of electrostatic charging, imagewise exposure and development is repeated multiple times on an electrophotographic photosensitive layer is applicable for color printing processes in which images are fixed onto the photosensitive material and is also capable of use in a transfer process in which three color or multicolor toner images are transferred onto another image receiving material. The electrophotographic process may be carried out according to the following sequence:

A photosensitive layer having a spectral sensitivity distribution wherein over a portion or a region of the wavelength range it exhibits low photosensitivity is subjected to the successive steps of electrostatic charging, imagewise exposure to form an electrostatic latent image thereon and development with toner to render the image visible. Preferably, the first exposure is to a wavelength of light for which the photosensitive layer has high sensitivity to thereby insure dissipation of charge in nonimage areas. The toner employed during development may contain powdered photoconductive material spectrally sensitized for light of the wavelength region for which the photosensitive layer has low photoconductivity. After this first development step, the photosensitive layer is uniformly, electrostatically charged and subjected to a flush exposure with light of the wavelength region for which the photosensitive layer has low photoconductivity. The electrostatic charge placed on the layer during uniform charging is barely attenuated by the flush exposure since the layer has only limited photoconductivity in this wavelength region. However, the surface potential in the toner image portions is lowered since the toner exhibits photosensitivity to the light of the wavelength region and the toner absorbs light generating a charge carrier and accordingly the charge on the toner image portions is neutralized. This lowering of the surface potential in the toner image portions is proportional to the amount of toner present on the photosensitive layer. The decay of the surface potential is therefore large in portions of the photosensitive layer bearing large amounts of toner and small in portions having small amounts of toner deposited thereon.

It is known that the sensitivity of a photosensitive layer becomes higher as a surface potential resulting from electrostatic charging thereon is lower. Consequently, the amount of toner adhering to said photosensitive layer in the succeeding development decreases in the portions where the amount of toner already present is larger. The attenuation of surface potential of the photosensitive layer due to the photosensitivity of the toner can be regulated by the amount of flush exposure. In addition, since the

amount of the attenuation of surface potential is governed by the amount of the toner, the correction is automatically controlled by the image formed on the photosensitive layer and does not require additional special regulation even in the situation of images in which highlight or shadow parts are predominant. The photosensitive layer having the surface potential lowered imagewise according to the previously deposited toner pattern is exposed to the second or next image followed by development with the second toner of appropriate color which may also contain powdered photoconductive materials sensitized for the spectral region in which the photosensitive layer has low photoconductivity. The density of the second toner image is decreased in accordance with that of the first toner image. In the situation, for example, of developing with photoconductive cyan toner and successively developing with photoconductive magenta toner and yellow toner, the amount of magenta color which is decreased in accordance with the undesirable absorption of the green light by the cyan toner to automatically correct the undesirable absorption of cyan toner. In a similar fashion, the amount of yellow toner which absorbs blue light that is deposited is decreased according to the amount of deposited cyan and magenta having undesirable absorptions in the blue light region to automatically correct the undesirable absorptions of cyan and magenta toner. The degree of correction may be readily controlled by the artisan by adjusting the amount of light during uniform exposure. It is not necessary that the toner to be employed in the last development step contains photoconductive material.

The invention may be further illustrated by reference to the accompanying drawing which shows the relationship of sensitivity (or photoconductivity) with respect to the wavelength of light. In this figure, 1, 2 and 3 are the spectral sensitivity of a photosensitive layer, for example, zinc oxide suitably sensitized with the dye, while 4 is a spectral sensitivity of photoconductive material contained in the toner which may, for example, also be dye sensitized zinc oxide. The spectral distribution of the light source to be employed for the flush exposure used to lower the surface potential of the photoconductive toner image is shown by curve 5. The discontinuity of sensitivity is conveniently provided between the sensitivity bands of 500-600 $m\mu$ and 650-700 $m\mu$. The discontinuity of course, could be provided in another part of the visible spectrum.

The photoconductive powder contained in the toner may have a spectral sensitivity in the wavelength region where the photosensitive layer has a low photoconductivity which exhibits two or more peaks instead of one peak. In this instance, the amount of masking in each step may be controlled independently by changing the ratio of exposure for these peaks. Preferably, when the imaging process is completed and a multicolor image has been reproduced, the sensitized photoconductive powder is bleached in order to remove coloration in the nonimage part of the photosensitive layer. Alternatively, the photoconductive powder itself may be removed by dissolving it in a suitable solvent.

It is not necessary that the photosensitive layer be sensitized for three colors. It is sufficient, for example, to sensitize the layer for only one color. In this case, it is sufficient to sensitize the photoconductive powder and the toner against the wavelength region for which the photosensitive layer has no photoconductivity. It becomes necessary, however, to employ an original image having optical density in the wavelength region where the photosensitive layer is sensitive, since exposure by direct color separation cannot be employed in this case.

The photosensitive imaging surface employed may be selected from known photosensitive materials including materials which may be sensitized or unsensitized to provide a discontinuity in sensitivity so that there is a portion of the light spectrum at which they exhibit low photoconductivity. No advantage is seen in enumerating each of the well known numerous materials as the artisan

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may readily select suitable materials. From this large group of known materials, zinc oxide is particularly preferred since it is capable of readily being sensitized in various wavelength ranges. Similarly, the photoconductive material that may be employed as a constituent of the toner may be selected from the known materials including those which may be sensitized or unsensitized to provide photoconductivity in a narrow portion of the visible spectrum. Given a photosensitive member having low photoconductivity with respect to a minor portion of the visible spectrum and high photoconductivity for a major portion of the visible spectrum, the artisan may readily select suitable photoconductive materials for the toner which, while unsensitized or while being sensitized, exhibit high photoconductivity in the minor portion of the visible spectrum. Zinc oxide is also a preferred material for use as the photoconductive particle in the toner because it is capable of being sensitized in a number of relatively narrow regions of wavelength.

With the use of zinc oxide and its capability of readily being sensitized, the ability to control the area of low photoconductivity on the photosensitive layer and the corresponding high photoconductivity in the relatively narrow band in the toner material, the artisan may select any suitable appropriate dye. In addition, the selection of to the area of low photoconductivity for the photosensitive layer. Knowing the region of low photoconductivity of the photosensitive layer either present or desired, one may provide dye sensitized zinc oxide particles by selecting any suitable appropriate dye. In addition, the selection of suitable dyes for dye sensitized toner materials may be readily selected by the artisan. Typical dye sensitizers include: tartrazine, erythrosin, brilliant milling green B (C.I. Acid Green 9), bromochlorophenol blue.

Development of the electrostatic latent image formed in each of the imaging sequences may be accomplished with any of the conventional development techniques. Included within this grouping of well known development techniques are: cascade development, as generally described in U.S. Pat. 2,618,551, magnetic brush development as generally described in U.S. Pat. 2,874,063, powder cloud development as generally described in U.S. Pat. 2,784,109, and liquid development as described in U.S. Pat. 2,877,133. The toner and materials employed in the dry development techniques described may be selected from the numerous materials which are known in the art. In providing the toner materials, it is necessary only that the artisan consider the color of the toner required in each of the development sequences. Typically, the toner materials are selected from conventional thermoplastic and thermosetting resins.

Development, according to the liquid development technique is particularly effective in producing the multi-color images from a multiple development technique according to the electrophotographic process of the invention. In this technique, a toner is dispersed in an electrically insulating liquid which is brought into contact with the photosensitive layer having the electrostatic latent image thereon and the toner separates from the insulating liquid and deposits on the photosensitive layer in accordance with the charge pattern.

Any suitable well known insulating liquid may be employed as the vehicle for the toner particles which may contain photoconductive particles. Typical well known materials have volume resistivities greater than about 10^{10} ohm-cm. so as not to effect the electrostatic charge pattern on the insulating layer and low dielectric constants of less than about 3.4. Typical specific vehicles include among others, the nonpolar hydrocarbons and hydrocarbon derivatives such as benzene, kerosene, cyclohexane, toluene, and carbon tetrachloride. As previously discussed, the photoconductive particles that may be employed in the toner particles may be selected from the well known conventional materials which may be mixed with materials suitably colored to provide the desired color in each

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of the development sequences. As is well known, the toner may be pigmented or dyed to provide this desired color. Typical of the numerous pigments known in the art are: phthalocyanine, benzadine yellow and brilliant carmine 6B.

DESCRIPTION OF PREFERRED EMBODIMENT

The following preferred example further defines and describes preferred materials, methods and techniques of the present invention. Unless otherwise indicated, all parts and percentages in the example are by weight.

EXAMPLE I

To five parts by weight of photoconductive zinc oxide powder are added tartrazine, erythrosin and brilliant milling green B (C.I. Acid Green 9), in a ratio of 1 mg. of dye to 10 g. of zinc oxide, in order to sensitize the zinc oxide against blue light region (430–500 $m\mu$), green light region (520–580 $m\mu$) and red light region (635–680 $m\mu$) respectively. The sensitized zinc oxide is dispersed in 1 part by weight of a composition consisting of styrene-alkyd resin and polyisocyanate hardener therefor. The dispersion obtained is applied to paper, which has been soaked in a solution of hygroscopic material in order to render the paper electroconductive, to obtain a coating about 10 μ thick after drying. The complete photosensitive paper is obtained after drying.

The prepared photosensitive paper is then electrostatically charged in the dark by negative corona discharge to a surface potential of 200 v. Successively, the photosensitive paper is exposed imagewise to an original image through a color slide and a red filter to form an electrostatic latent image. The image is developed with cyan developer prepared by the procedure described below. The photosensitive paper is again electrostatically negatively charged to a surface potential of 200 v. The photosensitive paper is subjected to a flush exposure through a filter having a peak transmittance of about 620 $m\mu$ thereby lowering the surface potential in the portions of cyan toner image by means of the photoconductive powder contained therein. The photosensitive paper is barely responsive to the light having an intensity maximum at 620 $m\mu$. The photosensitive paper in register with the position during the preceding exposure is subjected to imagewise exposure through the same color slide and a green filter to obtain a second electrostatic latent image, which is then developed with the magenta developer described below. After fixing, the photosensitive paper is similarly subjected to the steps of electrostatic charging, flush exposure with light having an intensity maximum at 620 $m\mu$. The photosensitive paper in register with the position during the preceding exposure is imagewise exposed through the same color slide and a blue filter and developed with the yellow developer described below to obtain a three color image thereon. The paper is dipped in a bleaching solution in order to remove the coloration in the nonimage part of photosensitive layer. A very clear color image on a white background is obtained.

The developer and bleaching solution employed in this process are prepared as follows:

(1) Liquid developer containing cyan toner: Liquid developer containing cyan toner is obtained by mixing solutions A and B of following compositions in a ratio of 4:1.

Solution A:

Phthalocyanine blue: 0.4 g.
Varnish obtained by heating rosin-denatured phenol-formaldehyde resin and linseed oil: 0.8 g.
Polymerized linseed oil: 1.0 g.
Cyclohexane: 800 ml.
Kerosene: 200 ml.

Solution B (Developer containing photoconductive toner):

Photoconductive zinc oxide on which bromochlorophenol blue is absorbed: 0.4 g.
Soybean oil-denatured alkyd resin: 1.0 g.
Linseed oil: 1.0 g.
Cyclohexane: 800 ml.
Kerosene: 200 ml.

Bromochlorophenol blue, which is capable of spectral sensitization for the wavelength range of 500–650 mμ, was absorbed by photoconductive zinc oxide in a ratio of 0.0001 part by weight in 1 part by weight of zinc oxide by means of treatment in methanol. The liquid developer obtained containing cyan toner is charged positively.

(2) Liquid developer containing magenta toner: Liquid developer containing magenta toner is prepared by mixing solution C of following composition and solution B described above in the ratio of 4:1.

Solution C:

Brilliant carmine 6B: 0.4 g.
Varnish obtained by heating rosin-denatured phenol-formaldehyde resin and linseed oil: 0.8 g.
Polymerized linseed oil: 0.6 g.
Linseed oil: 5 ml.
Cyclohexane: 800 ml.
Kerosene: 200 ml.

(3) Liquid developer containing yellow toner: In this developer, the use of photoconductive toner is unnecessary since this is to be employed in the last development.

The composition of liquid developer containing yellow toner is as follows:

Solution C:

Benzidine yellow: 0.3 g.
Soybean oil-denatured alkyd resin: 0.5 g.
Polymerized linseed oil: 0.2 g.
Varnish obtained by heating rosin-denatured phenol-formaldehyde resin and linseed oil: 1.4 g.
Cyclohexane: 800 ml.
Kerosene: 200 ml.

(4) A bleaching solution which is inactive against the toner, but is capable of dissolving sensitizing dyes contained in toner and photosensitive layer is prepared by mixing 1 part by volume of methanol and 1 part by volume of acetone and heating to 40° C. when in use.

Although specific materials and operational techniques are set forth in the above exemplary embodiment using the developer composition and development techniques of this invention, they are merely intended as illustrations of the present invention. There are other developer materials and techniques than those listed above which may be substituted for those in the examples with similar results.

Other modifications of the present invention will occur to those skilled in the art upon a reading of the present disclosure which modifications are intended to be included within the scope of this invention.

What is claimed is:

1. An electrophotographic process for producing a multi-color reproduction of an original colored object comprising the steps of:

(a) forming an electrostatic latent image corresponding to one of the primary colors on a photoconductive insulating layer having high photoconductivity for light of wavelength of a portion of the visible spectrum and low photoconductivity at least in part of the remaining wavelength range;

(b) developing said electrostatic latent image with a

toner complementary to the primary color and which has high photoconductivity for light of the wavelength for which the photoconductive insulating layer has low photoconductivity;

(c) forming an electrostatic latent image corresponding to a second primary color;

(d) developing said second electrostatic latent image with a toner complementary to the second primary color and which has high photoconductivity for light of the wavelength for which the photoconductive insulating layer has low photoconductivity provided that prior to development the photoconductive insulating layer is uniformly exposed to radiation of a wavelength for which the toner has high photoconductivity and the photoconductive insulating layer has low photoconductivity;

(e) forming an electrostatic latent image corresponding to a third primary color;

(f) developing said third electrostatic latent image with a toner complementary to the third primary color provided that prior to development the photoconductive insulating layer is uniformly exposed to radiation of a wavelength for which the toner has high photoconductivity and the photoconductive insulating layer has low photoconductivity.

2. The method of claim 1 wherein said photoconductive insulating layer comprises zinc oxide.

3. The method of claim 2 wherein said zinc oxide is dye sensitized to exhibit high photoconductivity for light of a wavelength of a major portion of the visible spectrum and low photoconductivity for light of a wavelength of a minor portion of the visible spectrum.

4. The method of claim 1 wherein said toner comprises zinc oxide.

5. The method of claim 4 wherein said zinc oxide is dye sensitized to exhibit photoconductivity for light of the wavelength for which the photoconductive insulating layer has low photoconductivity.

6. The method of claim 1 wherein said toner is dispersed in an insulating liquid to provide a liquid developer.

7. The method of claim 1 wherein each of said electrostatic latent images are formed by uniformly charging the photoconductive insulating layer in the dark followed by exposure to color separation negatives of the colored object to be reproduced.

8. The method of claim 7 wherein said first exposure is to light of a wavelength for which the photoconductive insulating layer has high photoconductivity.

9. The method of claim 7 wherein the photoconductive insulating layer is uniformly exposed to light of a wavelength for which it has low photoconductivity after the second and third electrostatic latent images have been formed.

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